

~~645~~ 5  
667

# CANADA

## THE PATENT OFFICE

PATENT No. 483,214

ISSUED MAY 13, 1952

## Diaz Amino Printing Colors

William H. von Glahn, Loudonville, New York,  
U.S.A., assignor to General Aniline & Film Cor-  
poration, New York, New York, U.S.A.

Application October 10, 1944, Serial No. 518,212  
In the United States October 1, 1943, Priority  
entered under Patents, etc., Emergency Order,  
1939

4 Claims — No drawing

EXAMINER'S  
COPY  
DIV. 3

1

This invention relates to dye intermediates and dyes obtained therefrom. More particularly, it relates to printing compositions containing stabilized diazo compounds, together with coupling components and to the dyes derived by coupling the diazo compound with the coupling component.

The process of dyeing fabrics by means of a dye paste or composition containing the dye components which couple to form the dye is now well known in the art of applying azo dyes to textiles. The most successful of such dye pastes is one known to the art generally wherein the diazo compound has been stabilized against premature coupling by condensing the diazo with particular amines, thus forming water soluble diazo amino compounds.

The printing paste contemplated by this type of dyeing process is prepared by mixing the diazo amino compound and a coupling component, adding to the mixture sodium hydroxide solution in quantities sufficient to dissolve the components, and making up the mixture to a printing paste by adding thereto a thickening agent such as starch or gum tragacanth or a mixture of both and the necessary quantities of water. If desired, such other textile assistants as Turkey Red oil, dispersing agents and solvents may be added. The fabric is printed by application of the paste in the desired design, drying and introducing to an ager where it is subjected for a short time to the action of steam containing the vapors of volatile organic acids. In this step the acid splits the amine stabilizer from its combination with the diazo compound and permits the latter to couple with the coupling component present in the printing paste. Following this development of the print, it is rinsed, washed and dried. Alternative methods of development may be employed such as introducing the printed fabric to a bath containing an acid such as formic acid, acetic acid or oxalic acid which bath may also contain other assistants and penetrants.

Various diazotized arylamines have been stabilized by condensation with an amine in accordance with this process and the stabilized diazo compounds combined with coupling components in a dyeing paste. As coupling components, arylides of 2,3-hydroxynaphthoic acid and other aromatic-o-hydroxy-carboxylic acids have frequently been employed. It has now been discovered that new printing colors or ice colors, as they are sometimes called in the trade, which are very valuable for

commercial purposes because of their excellent fastness properties and ability to produce shades of great depth on the fiber can be obtained by employing the diazo compound of 1,5-dimethoxy-2-amino-4-chloro benzene or 1,5-diethoxy-2-amino-4-chloro benzene as the base. Stabilized diazo amino compounds derived from this base split very rapidly with organic acids without decomposition and thus produce the full shade of the ice colors on the fiber. These colors have excellent fastness properties. It is this discovery to which the invention of this application is directed.

According to the process of this application, the 1,5-dimethoxy (or 1,5-diethoxy)-2-amino-4-chloro benzene is diazotized in the usual manner and the diazo derived therefrom stabilized by condensing it in an alkaline medium with amino compounds, preferably with N-monoalkylamino acetic acids, N-alkyl-taurines, N-alkyl-glucamines, proline, 4- or 20 5-sulfo-2-amino benzoic acid or the N-monoalkyl derivatives of the latter sulfoamino benzoic acids. These stabilizing amino compounds will prevent the diazo compounds from coupling in alkaline medium, but will permit its coupling in acidic media. Specific examples of such amines include sarcosine, methyltaurine, N-methylglucamine, proline, 4-sulfo-2-amino benzoic acid and N-methyl (or ethyl)-4-sulfo-2-amino benzoic acid.

A large number of coupling components which do not contain solubilizing groups can be used in preparing the printing paste. Most suitable for the purpose of this invention are the arylamides of o-hydroxy-aryl carbonic acids, known to the trade as Naphthol AS compounds, and  $\beta$ -keto carboxylic acids. Particularly good results are obtained when using the arylides of 2,3-hydroxy-naphthoic acid, of 2-hydroxy-anthracene-3-carboxylic acid, of 2-hydroxy-carbazole-3-carboxylic acid, or 7-hydroxy- $\alpha$ -naphthocarbazole-6-carboxylic acid, of aceto acetic acid, of benzoyl acetic acid, and of terephthaloyl-bis-acetic acid. The coupling component obtained by the acid combination of a nitriline-diazo with 1,7-amino-naphthol may also be used to advantage.

While the final colors may be obtained by any of the processes for the application of ice colors known in the art, the most important use of the printing pastes contemplated by this invention is in printing according to the above mentioned method. The 40 printing paste is prepared by mixing a diazo amino

## 5

printed material was dried and then treated for a short time in an ager with live steam containing the vapor of a mixture of acetic and formic acids. The developed prints were then soaped for 5 minutes in a boiling  $\frac{1}{2}\%$  soap solution, rinsed in clear water and dried. The deep maroon shade of good fastness properties was obtained.

## Example VIII

A printing paste was prepared by mixing:

2.9 parts of diazo amino C  
 1.9 parts of the coupling component obtained by acid combination of o-nitraniline diazo with 1,7-amino naphthol  
 4.0 parts of cellosolve  
 24.0 parts of water  
 3.0 parts of sodium hydroxide solution 30%  
 65.0 parts of gum tragacanth

Cotton and rayon piece goods were printed on an engraved roller with this printing paste. The printed material was dried and then treated for a short time with live steam containing the vapors of acetic acid. The developed prints were then soaped for 5 minutes in boiling  $\frac{1}{2}\%$  soap solution, rinsed in clear water and dried. A rich, deep black shade of good fastness properties was obtained.

From the foregoing description and illustrative examples, it is apparent to those skilled in the art that many embodiments of this invention may be made without departing from the spirit and scope thereof. It is to be understood that no limitations are intended in the following claims except those which are specifically recited therein or are imposed by the prior art.

## 6

1. The composition of matter comprising a water soluble diazo amino compound containing as the diazo component a diazo compound selected from the group consisting of the diazo of 1,5-dimethoxy-2-amino-4-chloro benzene and 1,5-diethoxy-2-amino-4-chloro benzene, an alkali metal hydroxide, a thickener and a coupling component selected from the group consisting of arylamides of o-hydroxy aryl carbonic acids, arylamides of  $\beta$ -keto carboxylic acids, and the acid combination product of a nitraniline diazo with 1,7-amino naphthol.

2. The composition of matter comprising a water soluble diazo amino compound containing as the diazo component the diazo of 1,5-dimethoxy-2-amino-4-chloro benzene, an alkali metal hydroxide, a thickener and the 2,5-dimethoxy-4-chlor anilide of 2,3-hydroxy naphthoic acid.

3. The composition of matter comprising a water soluble diazo amino compound containing as the diazo component the diazo of 1,5-dimethoxy-2-amino-4-chloro benzene, an alkali metal hydroxide, a thickener, and the 4-chloro-2-toluidide of 2,3-hydroxy naphthoic acid.

4. The composition of matter comprising a water soluble diazo amino compound containing as the diazo component the diazo of 1,5-dimethoxy-2-amino-4-chloro benzene, an alkali metal hydroxide, a thickener, and diacetato-acet-o-toluidide.

W. D. HERRIDGE,  
 140 Wellington St.,  
 Ottawa, Ont.,  
 Patent Agent  
 of the Applicant.

## Claims:

35

EDMOND CLOUTIER, C.M.G., O.A., D.S.P., Queen's Printer and Controller of Stationery, Ottawa, 1952

*Note.—The application for a Patent has become void.*

*This print shows the Specification as it became open to public inspection on Oct. 6, 1932,  
under Section 91 (3) (a) of the Patents and Designs Acts, 1907 to 1928.*

# PATENT SPECIFICATION



Application Date: Oct. 4, 1932. No. 27,579 / 32.

413,257

Complete not Accepted.

## COMPLETE SPECIFICATION.

### The Manufacture of Stabilized Diazo Solutions.

We, I. G. FARBENINDUSTRIE AKTIEN-  
GESELLSCHAFT, a Joint Stock Company  
organised under the laws of Germany, of  
Frankfort-on-Main, Germany, do hereby  
5 declare the nature of this invention  
and in what manner the same is to be  
performed, to be particularly described  
and ascertained in and by the following  
statement:—

10 This invention relates to the manufacture  
of stabilized diazo solutions.

It is known that in diazo solutions as  
used in the manufacture of azo dyestuffs  
on the fibre, after standing for a more or  
15 less long time, this depending on the  
stability of the specific diazo compound,  
separations of decomposition products are  
formed, which very unfavourably influence  
the fastness to rubbing of the dyeing,  
20 especially in dyeing on apparatus.

In accordance with the present invention  
this drawback is overcome, i.e. the  
formation of these separations is pre-  
vented, by adding to the diazo solution a  
25 dispersing or emulsifying agent forming  
aqueous solutions which are stable  
towards acids. As dispersing or emul-  
sifying agents suitable for the purpose of  
this invention there may be mentioned by  
30 way of example: purified sulphite waste  
liquor, the reaction products of carboxylic  
acids of aliphatic, cyclo-aliphatic or  
aromatic-aliphatic nature with organic  
amino sulphonate acids, sulphonation pro-  
35 ducts of higher fatty acid amides the  
production of which products is described, for example, in specifications Nos. 341,053, 343,524, 343,899; furthermore, compounds which are obtain-  
40 able by introducing polyglycolether  
radicles containing 4 or more ethylene  
groups into organic compounds contain-  
ing one or more hydroxy-, carboxy- or  
amino groups, the production of com-  
45 pounds of this type being described in  
French Patent No. 727,202; or, finally,  
ester-like condensation products of higher  
molecular carboxylic acids and sulphonate

acids containing hydroxy groups, which  
products have been described, for example, in French Patent No. 705,081.

The quantity of the dispersing or emul-  
sifying agent respectively to be added  
may vary within wide limits; as a general  
rule it may be stated, however, that  
generally about 1 to about 3 grams cal-  
culated upon one litre of the diazo bath  
is sufficient. The solutions obtained  
according to this invention remain clear  
during the whole dyeing process and dis-  
play a very good stability for a prolonged  
time.

The invention is illustrated by the  
following example:—

#### EXAMPLE.

2 grams of 4-chloro-1-methyl-2-amino-  
benzene are diazotized in the usual  
manner with sodium nitrite and hydro-  
chloric acid; the acid reaction to Congo  
Red is neutralized by the addition of  
sodium acetate, and, after making up  
with water to one litre, one gram of oleyl-  
methyltaurine is added to the solution  
(prepared according to specification No.  
343,899, example 4). This diazo solution  
remains clear for a prolonged time while  
the diazo solution prepared in the same  
manner but without the addition of oleyl-  
methyltaurine exhibits even after a short  
time, say about half an hour to one hour,  
pink coloured, flocculent separations.

Instead of oleylmethyltaurine there  
may be used with the same result, for  
example, oleylhydroxyethane sodium sul-  
phonate (compare French Patent No.  
705,081), or the products obtainable by  
the action of 20 molecular proportions of  
ethylene oxide upon one molecular pro-  
portion of octodecylalcohol, or upon one  
molecular proportion of oleyl-alcohol  
(compare French Patent No. 727,702).

Having now particularly described and  
ascertained the nature of our said inven-  
tion and in what manner the same is to  
be performed, we declare that what we  
claim is:—

[Price 1:-]

1. Process for stabilizing diazo solutions by the addition of a dispersing or emulsifying agent forming aqueous solutions which are stable towards acids.

5 2. Process for stabilizing diazo solutions substantially as described in the example.

3. Diazo solutions stabilized by the addition of dispersing or emulsifying

agents forming aqueous solutions which are stable towards acids. 10

Dated the 4th day of October, 1932.  
(Sgd.) CARPMAELS & RANSFORD,  
Agents for Applicants,  
24, Southampton Buildings, London,  
W.C. 2.

Redhill: Printed for His Majesty's Stationery Office, by Love & Malcolmson, Ltd.—1934.